

Enhanced Adhesion of Conductive Coating on Plasma-Treated Polyester Fabric: A Study on the Ageing Effect

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ABSTRACT: In recent years, there has been growing attention on intrinsically conducting polymers, such as polypyrrole (PPy) because of the wide range of possible applications. Adhesion to other materials is a pending problem that could be tackled by enhancing the chemical affinity of the surface toward PPy coating. In this work, low-temperature plasma pretreatments were used for improving adhesion of PPy on polyester (PET) fabrics by changing the surface chemistry and generating a microscopically rough surface. Oxygen and argon plasmas were used to treat both sides of PET fabrics before PPy deposition by *in situ* chemical polymerization. Moreover, PPy depositions were performed 1 h, 1 week, and

1 month after the plasma treatments to study possible ageing effects. Different chemical/physical characterizations (contact angle, surface energy, atomic force microscopy, and X-ray photoelectron spectroscopy) showed the efficacy of plasma pretreatments in inducing wettability on PET fabrics and promoting adhesion of the PPy layer. The enhanced adhesion was confirmed by abrasion tests and subsequent surface resistivity and color measurements. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: adhesion; coatings; cold plasma; conducting polymers; polypyrrole

INTRODUCTION

Electrically conducting fabrics produced by deposition of thin layers of inherently conducting polymers (ICPs) on the fiber surface of fabrics and yarns have recently been proposed for applications in electrostatic dissipation and heating devices,^{1–3} sensors,^{4–6} storage devices and capacitors,⁷ microwave attenuation and EMI shielding,^{8–10} antimicrobial^{11,12} and fire protection.¹³ Polypyrrole (PPy) is one of the most promising candidates for producing electrically conducting fabrics with surface resistivities ranging from tens to millions Ω /square. PPy-coated fabrics were widely produced by *in situ* polymerization of pyrrole from water solution onto the surface of many kinds of textile materials. The most pressing technical issue is the low adhesion of the PPy layer to the fiber surface. PPy has shown excellent affinity to cellulose-based fibers^{14–16} and to treated animal

fibers (e.g., Hercosett wool and Basolan wool).^{2,17} On the contrary, the adhesion to synthetic fibers is poor, and few are reported in literature. Solvent treatments have recently been proposed for polyamide fibers.¹⁸ Alkali treatments were performed on polyester (PET) fibers before PPy deposition showing an increase in the amount of deposited PPy but fastness to rubbing slightly decreased because of the resulting surface roughness.¹⁹ Moreover, prolonged immersion of PET fabrics in the reactants did not improve abrasion fastness.²⁰

In recent years, two articles^{21,22} reported information about the improvement of ICP adhesion on textiles by plasma treatments.

Oh et al.²¹ performed plasma surface modifications with oxygen, ammonia, and argon on nylon 6 fabrics with the aim of improving the adhesion and rate of polymerization. Oxygen-plasma-treated nylon fabric retained the highest conductivity and polyaniline deposit. Oxygen was revealed as the most aggressive and effective plasma gas compared with ammonia and argon plasma. More recently, Garg et al.²² pretreated wool and PET fabrics using an atmospheric plasma glow discharge to improve the ability of the substrate to bond with PPy coating. Abrasion testing showed that plasma treatment resulted in an improved PPy adhesion to both the

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wool and PET fabrics. It was found that a helium and nitrogen mixture was far more effective than other gases (i.e., pure helium, helium/acetylene).

Our work focuses on low-temperature plasma surface modifications to improve the adhesion between PPy coating and PET fiber surface modifying hydrophilicity and surface energy of PET fabrics and to investigate the ageing effect. Before conventional *in situ* polymerization, the fabrics were exposed to argon and oxygen plasma treatments. In this field, a common issue is the low stability of the effects of plasma treatments over time to minimize the surface tendency to revert back to the untreated state (the so-called "ageing effect"). Usually, a significant loss of the properties achieved takes place in the first hour after the treatment, and a plateau is reached at longer storage time. In some cases, this problem could lead to technical limitations. To investigate if the ageing effect is a drawback for adhesion between PPy and PET, in this work, depositions were performed 1 h, 1 week, and 1 month after the plasma treatments.

The great advantage of vacuum plasma is the efficiency, reproducibility, and the possibility of performing many processes with the same equipment: surface activation, surface cleaning, etching, and plasma polymerization of compounds on the substrate surface without the production of wastes.

Oxygen plasma is usually considered the most efficient in enhancing adhesion of coatings, creating polar functional groups on the surface, altering the surface energy, and contact angle values of polymers substrates.^{23,24} To make the surface of a polymeric material hydrophilic, argon plasma can be used as well as oxygen even though it does not contain oxygen atoms. The oxidation reactions occur due to the formation of many carbon and oxygen radicals on the PET surface. These radicals are reactive enough to initiate chemical reactions (e.g., oxidation) that finally lead to the creation of hydroxyl and carboxyl groups on the fabric surface.²⁵

Atomic force microscopy (AFM) was used to study the morphology of the plasma-treated textiles while X-ray photoelectron spectroscopy (XPS) was used to follow the changes in the surface chemical composition of the fabrics due to its interaction with plasma. Moreover, a drop shape analysis system allowed us to investigate the effect of plasma treatment on contact angle, surface energy, and wettability. Properties such as surface resistivity, abrasion resistance, and change in color were assessed for the coated fabrics.

EXPERIMENTAL

Materials

The substrate used was PET ISO-F04 Type 54 Dacron woven fabric, weight 140 g/m². The chemicals were:

TABLE I
Summary of the Plasma Conditions

Sample	Gas	Time (s)	Power (W)
Ox15/80	Oxygen	15	80
Ox60/80		60	80
Ox15/160		15	160
Ar15/80	Argon	15	80
Ar60/80		60	80
Ar15/160		15	160

Pyrrole (97%) by Fluka, Germany, Iron (III) sulfate hydrate (humidity 21%, Fe 21%–23%) by Riedel-de Haën and 2,6-Naphthalenedisulfonic acid disodium salt 97% (NDS) by Sigma-Aldrich, Germany. All chemicals were used without further purifications. Gases for plasma treatments were argon (99.9995%; Siad S.p.A., Italy) and oxygen (99.999%; Siad S.p.A., Italy)

Plasma equipment and treatment

Plasma was produced inside a stainless steel reactor (25 cm in height and 65 cm × 40 cm) with a parallel plate configuration (the upper electrode is grounded). PET fabrics (30 cm × 30 cm) were positioned on the lower electrode. Gases were uniformly distributed in the reactor chamber by the upper showerhead electrode (with pinhole diameter of 1 mm). The system is externally connected through an impedance matching network (PFM 1500 A, HÜTTINGER Electronic, Germany) to a 13.56 MHz radio frequencies (RF) power supply (PFG 600 RF, HÜTTINGER Electronic, Germany). The working pressure was kept constant at about 50 Pa, evacuating the chamber by means of a turbomolecular pump (Turbo-V 301 Navigator, VARIAN Vacuum Technologies, USA) and a rotary pump (DS 602, VARIAN Vacuum Technologies, USA) and measuring the pressure with a capacitive manometer (Baratron Type 626A, MKS Instruments, USA) and a gauge controller (senTorr CC2C, VARIAN Vacuum Technologies, USA). Plasma surface modification took place at an RF power of 80 W and treatment times of 15 and 60 s for each fabric side. Moreover, a test was performed using a higher discharge power (160 W) for a short period of time (15 s). The samples were labeled as indicated in Table I.

PPy coating

Plasma-treated fabrics were stored for 1 h, 1 week, and 1 month at 20°C and 65% relative humidity (RH). After that time, the fabrics were cut into squares of 15 cm × 15 cm for *in situ* PPy chemical deposition. PPy depositions were performed at room temperature by plunging the samples in stirred solutions of ferric sulfate (82 mM) and NDS (15 mM) with a liquor ratio of 50 : 1 mL/g. After an impregnation of 5 min,

pyrrole was added dropwise to the solution, up to the final concentration (75 mM). The samples were removed from the polymerization bath after 4 h, rinsed in cold water, dried overnight at room temperature, and stored at 20°C at 65% RH for 24 h before further tests. The samples were labeled as “1h”, “1w,” and “1m” depending on the time passed between plasma treatment and PPy coating, namely: 1 h, 1 week, and 1 month. If not reported, 1 h had passed between plasma treatment and PPy coating. PPy uptake was measured by weight differences before and after coating.

Contact angle and wettability

Contact angle and wettability of untreated and plasma-treated samples were investigated by a DSA20E “Easy-drop standard” drop shape analysis system produced by Krüss, Germany, using the sessile drop method. Measurements were performed in a conditioned laboratory (20°C and 65% RH). Distilled water drops were deposited on the fabric surface by means of a software-controlled dosing system and a glass syringe. The contact angles were the average of at least eight measurements for each sample, and standard deviation values were determined. The evaluation of the drop image was performed with the DSA1 software included and, due to the fast absorption rate of treated PET fabrics, a high speed CCD CF4016 camera was used to record videos at 149 fps and calculate wettability times.

XPS

XPS of untreated and plasma-treated samples were obtained with a PHI 5000 Versa Probe system (Physical Electronics, MN, USA) using a monochromatic Al radiation at 1486.6 eV, 25.6 W power, with an X-ray beam diameter of 100 μm. The energy resolution was about 0.5 eV. XPS measurements were performed at a pressure of 1.0×10^{-6} Pa. The pass energy of the hemisphere analyzer was maintained at 187.85 eV for survey scan and 29.35 eV for high-resolution scan, while the takeoff angle was fixed at 45°. As the samples are insulators, an additional electron gun and an Ar⁺ ion gun were used for surface neutralization during the measurements. Binding energies of XPS spectra were corrected by referencing the C1s signal of adventitious hydrocarbon to 285 eV. XPS data fittings were performed with PHI multipakTM software using the Gauss-Lorenz model and Shirley background. XPS analysis was performed 1 month after the plasma treatments.

Microscopy

Morphological changes of the plasma-treated fabrics were studied by means of a Nano-R2 AFM produced by Pacific Nanotechnology, USA and were evaluated

from 4 μm² images. The AFM imaging technique used was Close Contact mode and APPNANO (USA) highly doped single crystal silicon probes of 125 μm nominal length were used. Data were acquired by means of SPM Cockpit Software, processed and analyzed by Nanorule+ software, both equipped with the Nano-R₂ system.

Abrasion tests

Abrasion tests were performed using a Nu-Martindale Abrasion and Pilling Tester produced by James Heal & Co. (UK), according to EN ISO 12947 standard method. Two kinds of abrasion tests were performed: (a) for subsequent electrical measurements, round specimens with a diameter of 15 cm were cut from the PPy-coated samples and subjected to abrasion cycles with a load of 9 kN; (b) for subsequent color measurements, round specimens with a diameter of 3.9 cm were submitted to abrasion without the load. The procedures were previously described in several articles.^{2,20,22}

Electrical measurements

Electrical measurements were performed on fabrics sample (abraded or not) cut into squares of 10 cm × 10 cm at 20°C and 65% RH with an Amersham EPS2A200 generator produced by General Electric Company, USA. As the temperature influences the resistivity of conducting materials, an electrical power of 1.0 W (DC) was applied. In this way, the samples reached almost the same temperature by Joule effect heating. Temperature measurements were performed using a FLIR i7 infrared camera (Extech Instruments, USA). The mean temperature reached was $25.0 \pm 0.5^\circ\text{C}$. The generator gives voltage and current values. The surface resistivities were calculated by Ohm’s law. The equations involved are:

$$P = V \times I \quad (1)$$

$$V = R \times I \quad (2)$$

$$\rho_s = R \times D/L \quad (3)$$

where P is the electrical DC power (in W), V is the voltage (in V), I is the current (in A), ρ_s is the surface resistivity (in Ω/sq), D is the sample width (in cm), and L is the sample length (i.e., the distance between electrodes, in cm). Considering that the samples are squares ($D = L$), the relation between electrical power and surface resistivity obtained from eqs. (1)–(3) is given by the following eq. (4):

$$\rho_s = P/I^2 \quad (4)$$

Color measurements

Color measurements were performed on PPy-coated plasma-treated and untreated fabrics, before and after

TABLE II
Contact Angle Measurements, Surface Energy, and
Wetting Time Values of Untreated and Plasma-Treated
Fabrics (No Sample Ageing)

Sample	Contact angle (degree)	Surface energy (mJ/m ²)	Wetting time (ms)
Untreated	123.7 ± 1.8	32.4	85,600
Ox15/80	70.5 ± 1.9	97.1	637
Ox60/80	55.1 ± 2.2	114.5	463
Ox15/160	44.3 ± 4.5	124.9	282
Ar15/80	63.7 ± 2.5	105.1	1928
Ar60/80	54.9 ± 3.5	114.7	346
Ar15/160	61.0 ± 2.6	108.1	1133

abrasion tests, with a Datacolor (Switzerland) Spectraflash SF600XV spectrophotometer, under CIE standard illuminant D65 and a 10° observer. The data obtained from color measurements were reprocessed and converted into 8-bit grayscale images representing the samples. The change in color from the starting black of PPy-coated samples to the gray of abraded samples and the different gray level intensities were related to the loss in conductive performances of the PPy-coated fabrics due to abrasion.

RESULTS AND DISCUSSION

Contact angle and wettability

The results of the wettability and surface contact angle tests for PET fabrics after plasma treatments are shown in Table II. All the plasma treatments considerably reduced the contact angle and wetting time of the PET fabric. In particular, etching reaction with O₂ gas at 160 W for 15 s is the best combination to reduce the contact angle and improve the wettability of PET fabric. As far as argon is concerned, the best results were achieved with a 60 s treatment performed at 80 W. After 1 week, an increase of contact angle on the treated samples (ranging from 17.1% of Ox15/160 to 28% of Ar15/80) was found as shown in Table III, indicating an "ageing" behavior^{24,26} due to a loss of some of the functional groups introduced with oxygen and argon plasma treatments. There can be various reasons for the ageing effect such as a reorientation of polar groups at the surface or the reaction of free radicals from the atmosphere to the surface.²⁴ Taking into consideration the high contact angle value of untreated PET, the ageing effect did not completely eliminate the great improvement in wettability induced by the plasma process. Measurements were repeated after 1 month, but no further significant variations of contact angle values were found (Table III), demonstrating a stabilization of the treated surfaces.

Surface energy

Surface energy was calculated by using the Young-Duprè equation.²² Table II shows that the calculated

surface energy values increase for all treated samples compared with the untreated one ($E = 32.4$ mJ/m²). The highest value was obtained for the sample treated at 160 W for 15 s with O₂ plasma ($E = 124.9$ mJ/m²). The change of surface energy after plasma treatments is probably due to the formation of hydrophilic groups. As found in literature,²⁷ increases in surface energy are mainly due to the presence of polar groups such as C—O, O=C—O, and C=O. The surface energy data are in accordance with wettability and contact angle results: the decrease of contact angle can also be explained by means of dominant increase of the polar force of the surface free energy of the modified polymers.²⁷

XPS

XPS investigation allows us to highlight the effect of plasma treatment on PET fabrics. The analysis of Survey Scan data (Table IV) shows an increase of O/C atomic ratio for all plasma-treated samples compared with the untreated one. Moreover the peaks that correspond, respectively, to C—O (286.5 eV) and O=C—O (289 eV) bonds, significantly increase (Table V) in the treated samples indicating a bond scission and incorporation of oxygen into the PET surface and thus to the formation of additional functional groups²⁴ that cause the increase of surface energy, as shown before. These results suggest that an etching process took place due to the interaction of plasma species with the PET fabric surface.

AFM

To assess the relation of contact angle and surface free energy to surface roughness, AFM analysis was

TABLE III
Variation of Contact Angles with Ageing

Sample	Contact angle (degree)	
Untreated	123.7	
Ox15/80	1h	70.5
	1w	86.2
	1m	86.4
Ox60/80	1h	55.1
	1w	65.6
	1m	65.2
Ox15/160	1h	44.3
	1w	51.9
	1m	52.0
Ar15/80	1h	63.7
	1w	81.5
	1m	81.0
Ar60/80	1h	54.9
	1w	67.0
	1m	67.2
Ar15/160	1h	61.0
	1w	72.9
	1m	73.0

TABLE IV
C1s, O1s Element %, and O/C Ratio % of the Plasma Treated and Untreated PET Fabrics

Survey scan	Sample						
	Untreated	Ox15/80	Ox60/80	Ox15/160	Ar15/80	Ar60/80	Ar15/160
C1s	74.4	70.3	68.7	68.2	71.2	67.9	68.7
O1s	23.4	29.0	30.5	30.7	27.0	29.3	28.2
O/C	0.31	0.41	0.44	0.45	0.38	0.43	0.41

performed. Oxygen and argon plasma-treated samples showed similar topographical changes. Figure 1 reports AFM images of untreated and oxygen and argon plasma-treated fabrics. The surface of the untreated sample is relatively smooth [Fig. 1(a)]. After the plasma treatment, pits and bumps are visible resulting in a rougher surface. This determines an increase of the surface area and thus a better wettability. Moreover, AFM pictures show that plasma operating conditions (i.e., treatment time and RF power) can influence the extent of surface modifications. An increase in roughness (higher dimension and number of protuberances) had been created on the surface by etching as the treatment time increases from 15 to 60 s at the same power (80 W), [Fig. 1(b,c)]. Figure 1(d) shows an evident ablation and physical removal of surface fragments produced by a discharge power of 160 W for just 15 s. Figure 1(e–g) (Ar 15/80, Ar 60/80, and Ar 15/160, respectively) of Argon plasma-treated surfaces are shown for comparison.

Surface roughness was measured by image analysis of $4 \mu\text{m} \times 4 \mu\text{m}$ areas and expressed as root-mean-square (RMS). As reported in Figure 2, increases of surface roughness were found for all treated samples in comparison with untreated PET fabric. In particular, at 80 W of discharge power an increase of RMS values with exposure time for both gases was observed. An increase of surface roughness is also observed for the 15 s treatments with O₂ and Ar increasing the discharge power from 80 to 160 W. The more evident surface modification occurred to O₂ treated sample at 160 W for 15 s: the RMS value of plasma-treated sample (165 nm) is significantly higher than the untreated sample (95.3 nm). These kinds of changes in surface roughness by plasma treatments are usually linked to improvements of wettability, adhesive properties, and bond-

ing strength of PET substrates.²⁷ The relevant change in surface topology is an important factor introduced by plasma action that is not influenced by the ageing effect. This probably contributes to keep the enhanced wettability of treated PET fabrics and thus favors the PPy deposition, immediately after plasma treatment (1 h) or after 1 week or 1 month.

Surface resistivity and abrasion tests

PET fabrics have surface resistivity in the range of $10^{12} \Omega/\text{sq}$.²⁸ Moreover, the fabric used in this work has different structure in weft and warp, because in weaving the highly tensioned warp threads resulted in a straight conformation, while the weft threads had to revolve around the warp threads theoretically resulting in $\pi/2$ times yarn length per fabric length unit. Therefore, different values of surface resistivity have been measured in weft and warp directions after coating with PPy. In particular, resistivities in weft direction are about 1.6 times greater than in warp direction.

Table VI reports results of the surface resistivity measurements. Plasma-treated fabrics show lower surface resistivities with respect to untreated fabrics in both weft and warp directions. No significant changes are noted relating to the different plasma treatment conditions tested, but all the treated fabrics show improvements of the electrical conductivity. The decreases of surface resistivity are of about $10 \Omega/\text{sq}$ in weft direction and about $3 \Omega/\text{sq}$ in warp direction, in average. PPy uptake is 17.4% in untreated fabrics, while $\sim 18\%$ of PPy uptake is measured in both oxygen and argon plasma-treated fabrics. As plasma treatments enhance the wettability of the fabrics, the polymerizing solution (containing monomer, oligomer, oxidant, and dopant ions) can easily penetrate into the empty spaces of the

TABLE V
High Resolution XPS of C1s Components (%)

Functional groups	Sample						
	Untreated	Ox15/80	Ox60/80	Ox15/160	Ar15/80	Ar60/80	Ar15/160
C-C C-H	79.9	59.2	50.19	61.91	64.67	56.5	60.1
C-O	12.98	28.63	37.32	24.37	25.2	31.58	29.82
O-C=O	7.12	12.16	12.49	13.72	10.1	11.92	10.09

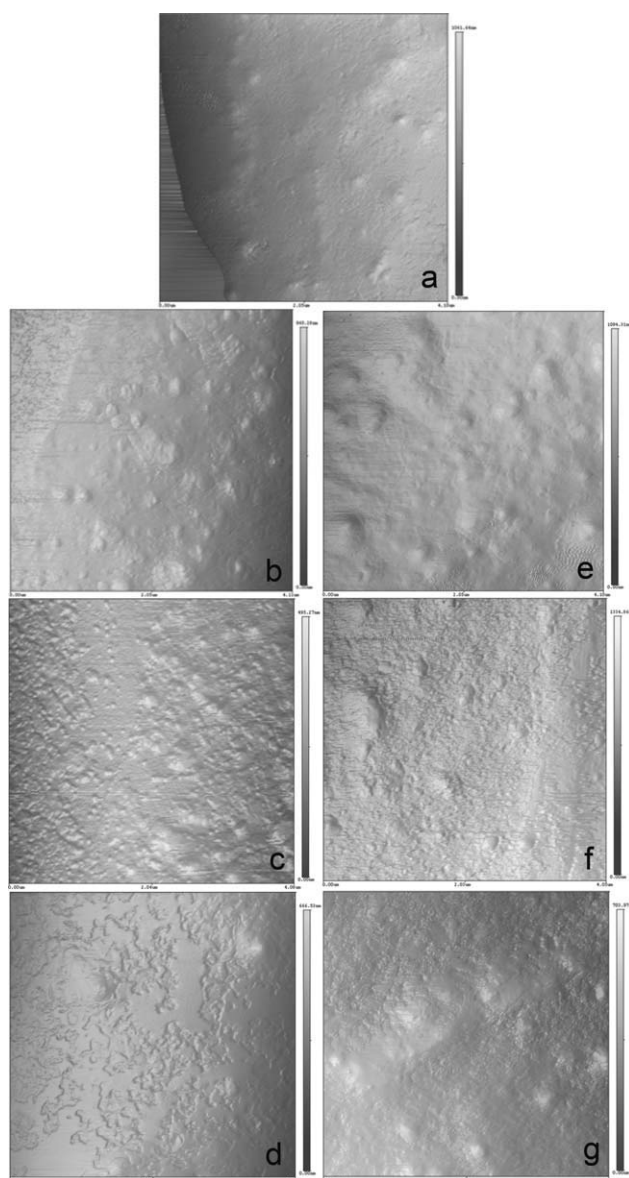


Figure 1 AFM images of untreated (a), Ox15/80 (b), Ox60/80 (c), Ox15/160 (d), Ar15/80 (e), Ar60/80 (f), and Ar 15/160 (g) PET fabrics.

fabric structure by capillary, and then the forming PPy layer can evenly cover the fiber surfaces also inside the yarns. Therefore, the resulting surface resistivity diminishes because the percolation pathway shortens. Moreover, the enhancement in conductivity is still evident in fabrics submitted to PPy deposition both 1 week and 1 month after the plasma treatments. This result is very interesting because it demonstrates the effectiveness of plasma pretreatment even after considerable storage times. Probably, this behavior is due to the combined chemical and morphological change of surface properties induced in plasma-treated fabrics.

In fact, as described above by XPS and AFM analysis, plasma not only chemically modifies the fiber

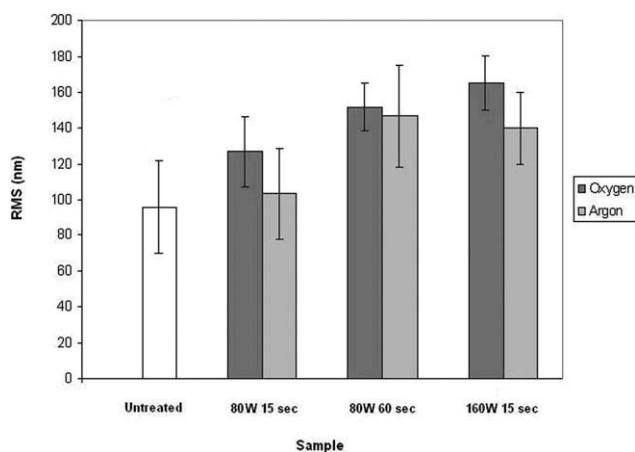


Figure 2 RMS values of untreated and plasma-treated fabrics.

surface introducing polar oxidized groups and favors the electrostatic adhesion of a positively charged polymer, such as PPy but also induces a change in the surface roughness that contributes to modify the wettability of the PET surfaces.

Figure 3 reports the measurements of surface resistivity of untreated and plasma-treated fabrics after abrasion tests. The data refer to fabrics coated with PPy 1 h after the plasma treatments. The plasma treatments strongly improve the stability of electrical property to abrasion. From this point of view, the best conditions are plasma with higher time (60 s) and lower power (80 W) or higher power (160 W) and lower time (15 s) for both oxygen and argon. In particular, it seems that at the same conditions, the

TABLE VI
Surface Resistivity Measurements

Sample		Surface resistivity (Ω/sq)	
		Weft	Warp
Untreated		70.6	44.4
Ox15/80	1h	62.0	40.6
	1w	63.1	39.6
	1m	62.0	42.7
Ox60/80	1h	60.1	40.1
	1w	61.1	38.6
	1m	61.0	39.1
Ox15/160	1h	60.1	40.2
	1w	57.4	39.6
	1m	62.0	41.1
Ar15/80	1h	63.0	41.6
	1w	61.9	42.2
	1m	58.3	41.1
Ar60/80	1h	64.0	42.7
	1w	59.2	42.2
	1m	61.0	41.6
Ar15/160	1h	61.0	41.1
	1w	57.4	40.6
	1m	57.4	41.6

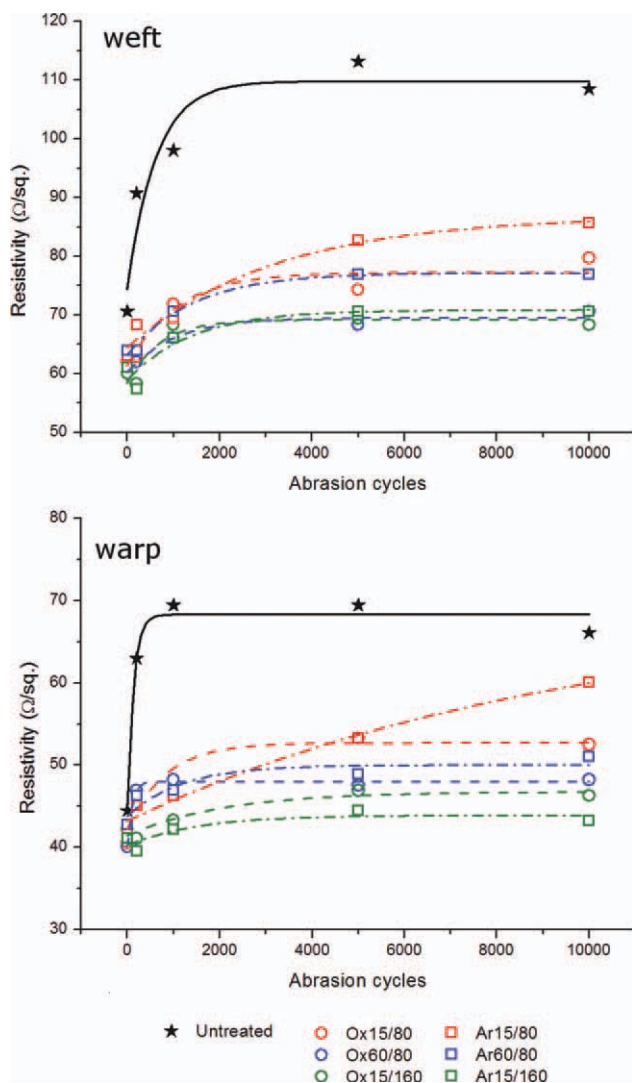


Figure 3 Surface resistivity of PPY-coated untreated and plasma-treated fabrics (1 h aged samples) after abrasion tests. Lines were drawn for eye-guide purpose only. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

improvement of adhesion obtained with oxygen plasma treatments is slightly higher than with argon. It is worth noting that the surface resistivity values of the fabrics Ar15/160, Ox15/160, and Ox60/80 subjected to 10,000 abrasion cycles were comparable with the resistivity of untreated fabric not subjected to abrasion.

Color measurements

Abrasion resistance is evident in the pictures in Figure 4 showing samples of untreated and oxygen plasma-treated fabrics after abrasion tests. The untreated fabric [Fig. 4(a)] shows high color change after just 50 abrasion cycles; on the contrary, the plasma-treated fabric [Fig. 4(b)] does not change in color also after 10,000 abrasion cycles.

More accurate and objective measurements about color changes were obtained performing color measurements after abrasion on PPY-coated untreated samples and treated samples PPY-coated 1 h, 1 week, and 1 month after plasma treatment. Figure 5 reports different graphs of the gray intensity of the 8-bit grayscale images obtained from the color measurement data reprocessing. Each graph compares the behavior of the PPY-coated untreated fabric after abrasion with that of PPY-coated plasma-treated fabrics. It is interesting to note that the results reported in graph (a) [Fig. 5(a)], related to treated samples in which the PPY-coating was performed 1 h after the plasma treatment, follows the same trend of the surface resistivity measurements reported above (in particular, see Fig. 3 for a comparison). The changes in color from black to lighter and lighter gray with increasing abrasion cycles can be used to give an indirect indication of the decrease of surface resistivity. All samples not subjected to abrasion are black and thus represented by low values of gray level (from 5 to 15). Higher values of gray level means higher level of loss in conductive performances due to the abrasion and removal of the PPY-coating. The bad performances of the PPY-coated untreated fabrics after abrasion are demonstrated by the high gray levels reached with increasing abrasion cycles: 70 after 200 cycles, 86 after 1000 cycles, up to 101 and 110 after 5000 and 10,000 cycles, respectively. Instead, lower changes in gray level intensity for all the plasma-treated samples demonstrate their better conductive performances, maintained also after thousands of abrasion cycles. Graph (a) shows that, amongst plasma-treated samples coated immediately after the treatment, the worst performance is that of the fabric pretreated in argon plasma for 15 s at 80 W. However, the gray level reached after 10,000 cycles (60) is far lower than that reached by the untreated fabric after only 200 cycles (70). Graphs (b) and (c) confirm the good stability of the treatment and the induced enhancement in conductivity

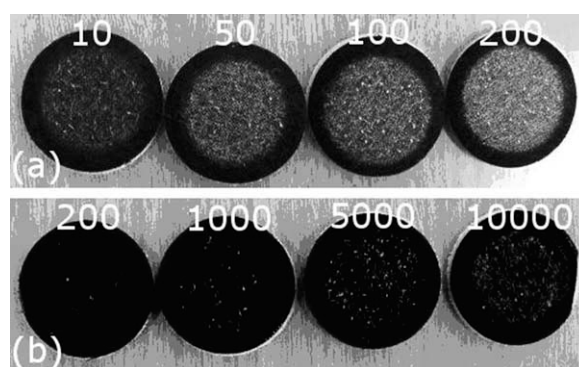


Figure 4 Pictures of abraded PPY-coated samples: (a) untreated fabrics and (b) Ox60/80 plasma-treated fabrics. Numbers are the abrasion cycles.

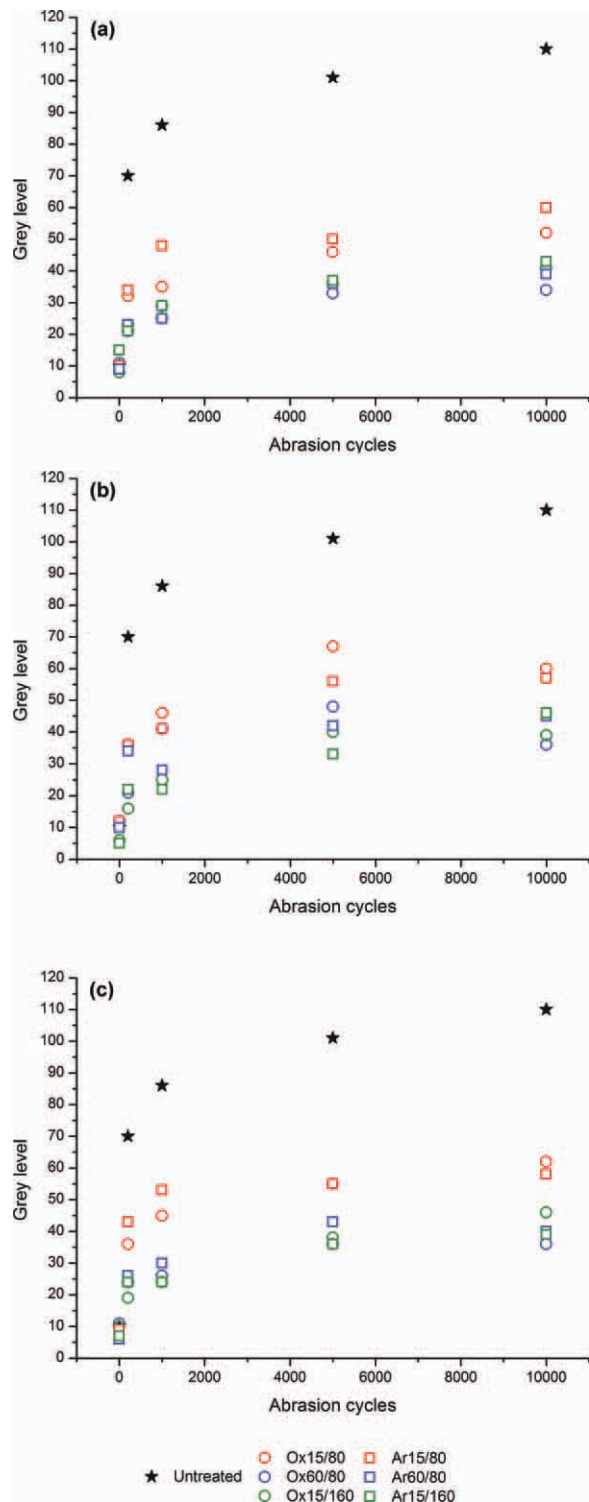


Figure 5 8-bit gray intensity level of PPy-coated fabrics after abrasion tests: (a) untreated vs. plasma-treated fabrics PPy-coated 1 h after plasma treatment; (b) untreated vs. plasma-treated fabrics PPy-coated 1 week after plasma treatment; (c) untreated vs. plasma-treated fabrics PPy-coated 1 month after plasma treatment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

during time even if an ageing effect was verified as reported in the contact angles measurement section.

Such characterization indirectly confirms that the plasma treatments strongly improve the stability of electrical property to abrasion and that the best performances are reached with higher time (60 s) and lower power (80 W) or higher power (160 W) and lower time (15 s) for both oxygen and argon.

CONCLUSIONS

The plasma treatments allowed the incorporation of polar functional groups onto the PET surface, as seen by XPS analysis. Improvements in wettability of the fabric have been shown by significant decreases in contact angle and increase in surface energy. Furthermore, AFM results showed an increase of PET surface roughness caused by plasma etching, related to operating parameters like treatment time and discharge power applied. The chemical/physical modifications introduced by plasma greatly improved the adhesion to the fabric of the electrically conducting coating resulting from the *in situ* oxidative polymerization of pyrrole in water solution. This enhanced behavior was confirmed by both surface resistivity measurements and colorimetric analysis after abrasion tests.

Results obtained showed also that the combined chemical and morphological effect of plasma treatment on the fabrics surface allowed us to maintain over time the enhanced wettability and to minimize the known issue of the “ageing effect.” This was particularly highlighted by the similar results obtained, in terms of conductivity and abrasion resistance, on PET fabrics coated with PPy after 1 h, 1 week, and 1 month after plasma treatment.

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